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## (54) Title of the Invention :

**Concentrated Wetting Liquid for the Planographics Process**

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**Description****1. Title of the Invention****Concentrated Wetting liquid for the Planographics Process****2. Scope of the Patent Application**

(1) Concentrated wetting liquid for the planographics process characterized by the fact that it includes the following components:

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(イ) about 0.05 to 10 wt % of the film formable, water soluble macromolecule.

(ロ) about 1 to 25 wt % of an alcohol, a glycol and / or a polyol which has 2 to 12 carbon atoms, and which is water soluble, or which can be made to be water soluble.

(ハ) about 0.2 to 50 wt % of at least one compound as the surfactant, selected from the group of ethylene oxide and / or the propylene oxide adduct of 2-ethyl-1, 3-hexane diol, and ethylene oxide and / or the propylene oxide adduct of acetylene glycol.

(ニ) about 0.01 to 20 wt % of a water soluble organic acid, inorganic acid, or a salt of these, and

(ホ) about 30 to 70 wt % of water.

(2) Wetting liquid composition characterized by the fact that the concentrated wetting liquid described in Claim 1 is diluted with water, and that the solid portion in the diluted liquid is made to be 0.01 to 3 wt %.

### 3. Detailed Explanation of the Invention

This invention relates to the concentrated wetting liquid that is useful for the offset lithography of the planographics process.

#### [Existing Technique and the Problem Which Should Be Solved]

The planographics process is the printing method which skillfully utilizes the nature of water and oil which fundamentally do not mix with each other, and the printing surface consists of the region which accepts the water and repels the oil based ink, and the region which repels the water and accepts the oil based ink, and the former one is the non-image region, and the later one is the image region. The desensitizer has the following function,

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namely, when the non- image region is wetted with the wetting liquid that includes the desensitizer, the boundary chemical difference between the image region and the non- image region is expanded, and the ink repelling nature of the non- image region, and the ink accepting nature of the image region, are increased. The desensitizers that have been known generally are, for example, the alkali metal salts of, or the ammonia salts of dichromic acid, phosphoric acid or its salts, for instance the ammonium salt, gum Arabic, or the aqueous solution which includes the colloidal materials such as calboxy methyl cellulose (CMC) etc.

However, the wetting liquid that includes these desensitizers, is difficult to wet evenly on the non- image region of the print, so that the printed material sometimes get soiled, and also quite a bit of skill is required to adjust the supplied amount of the wetting liquid.

In order to improve this situation, the "Darl glen?" (*phonetically written, Translator*) method has been suggested, in which an aqueous solution which includes about 20 to 25 % of iso propyl alcohol, is used as the wetting liquid. In this method, the wetability of the non- imaging part becomes good, and the amount of the wetting liquid can be small, and it is easy to adjust the balance of the supply of the printing ink and water, and the amount of the wetting liquid that emulsifies into the printing ink becomes small, and the transferring ability of the printing ink to the sheet becomes good, and thus, there are various advantages in the workability and the accuracy of the obtained printed material.

However, this iso propyl alcohol tends to evaporate easily, therefore, a special device is required to maintain the concentration of iso propyl alcohol in the wetting liquid to be constant, and this makes the cost high. In addition, iso propyl alcohol has a distinctive odor, and it has a problem with its toxic nature too, so that it is not preferred for use in the working environment.

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In addition, even if this wetting liquid that includes iso propyl alcohol is applied on the ordinary offset lithography that uses a water rod, the iso propyl alcohol evaporates on the roller and on the lithograph surface, so that the effect can not be obtained.

In addition, recently, the social opinion concerning industrial pollution is very strict, and the discharge regulations for the chromium ions in the waste water have become more strict, and the usage of organic solvents such as iso propyl alcohol, tends to be regulated from the safety and hygiene point of view. Therefore, the desensitizer which does not contain these has been desired.

In order to achieve these objectives, the compositions which include various surfactants are described in Patent Application Kokoku No. S55-25075, Patent Application Kokoku No. S55-19757, and Patent Application Kokoku No. S58-5797. However, in the case when these are used as the wetting liquid, in order to maintain the surface tension to be 35 to 50 dyne / cm, the concentration of the surfactant in the desensitizer must be maintained to be quite high. Also, in the actual planographics process, the water and ink are actively moving under the ink roll that rotates at high speed, the printing board, and the wetting liquid supply roll, therefore, there were some problems such as the occasional attaching of water on the ink film or the spreading of ink on the surface of the water, etc., however, the combinations of the suggested surfactants mentioned above, were not sufficient to solve these problems. In addition, the wetting liquid that includes these surfactants tends to bubble when it is transferred by a pump, or when it is stirred, and this was a disadvantage too.

US Patent No. 3,877,372 described the solution which contains a mixture of ethylene glycol mono butyl ether and at least one of hexylene glycol and ethylene glycol. US Patent No. 4,278,467 described the wetting liquid which contains at least one out of the group of n- hexoxy ethylene glycol, n- hexoxy di- ethylene glycol, 2- ethyl -1, 3- hexane diol, n-

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butoxy ethylene glycol acetate, n- butoxy di-ethylene glycol acetate, and 3- butoxy -2- propanol. Patent Application Kokai No. S57-199693 described the wetting liquid that includes 2- ethyl -1, 3- hexane diol and at least one from the group of the completely water soluble propylene glycol, ethylene glycol, di-propylene glycol, di- ethylene glycol, hexylene glycol, tri ethylene glycol, tetra ethylene glycol, tri propane glycol, and 1, 5- penta diol. These wetting liquid compositions do not contain iso propyl alcohol, therefore, it is advantageous from a safety and hygiene point of view, however, the wetting of the non-imaging part during printing is not really perfect for the PS board of the cathode aluminum oxide substrate, and especially during the high speed printing, soil is generated on the non- imaging part, or the shape of the dot imaging parts is not correct, and the dots become large and irregular, and therefore, it sometimes causes the so called "tangling" of the dot imaging parts. In addition, the solubility of 2- ethyl -1, 3- hexane diol in water is not sufficient, and it is disadvantageous for obtaining the concentrated wetting liquid or the additives for the wetting liquid in high concentration.

The objective of this invention is to offer at low cost the wetting liquid composition for the planographics process and the concentrated wetting liquid, which does not have the toxicity or disadvantages that the existing wetting liquids used to have, and with which a great deal of professional skill is not necessary to adjust the amount of the supply in the printing process, and of which the supply can be easily adjusted, and which not only can prevent the soiling or "bleeding" of the planographic plate which uses a support body that was electro chemically rough surfaced and in addition which was cathode oxidized, and also which has other advantages, such as it can be applied in the high speed printing such as in the off rotary printer, etc., and thus which has excellent wetting liquid characteristics and with which the high quality printed material can be easily obtained.

#### [Method to Solve the Problem]

The inventors of this invention investigated to achieve the above mentioned objectives,

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and they discovered that the above mentioned problems can be solved by using the wetting liquid composition that is described below for the planographic process, and this invention was made.

Therefore, this invention relates to the concentrated wetting liquid for the planographic process which includes the following components (イ) to (ホ), and also the method to use this liquid.

(イ) about 0.05 to 10 wt % of a film formable, water soluble macromolecule.

(ロ) about 1 to 25 wt % of an alcohol, glycol and / or polyol which has 2 to 12 carbon atoms, and which is water soluble, or which can be made to be water soluble.

(ハ) about 0.2 to 50 wt % of at least one compound as the surfactant, selected from the group of ethylene oxide and / or the propylene oxide adduct of 2-ethyl-1, 3- hexane diol, and ethylene oxide and / or the propylene oxide adduct of acetylene glycol.

(ニ) about 0.01 to 20 wt % of the pH buffer adjusting agent which consists of a mixture of a water soluble organic acid, an inorganic acid, or a salt of these, and

(ホ) about 30 to 70 wt % of water.

Next, this invention will be explained in detail.

The film formable, water soluble macromolecule that is used in this invention (component (イ)) gives the hydrophilic nature to the non- imaging region of the planographic print board.

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The concrete examples of the preferred macromolecule are for instance, gum Arabic, starch derivatives (for example, dextrin, enzyme decomposed dextrin, hydroxy propylated enzyme decomposed dextrin, carboxy methylated starch, phosphoric acid starch, octenyl succinated starch), salts of alginic acid, cellulose derivatives (for example, carboxy methyl cellulose, carboxy ethyl cellulose, hydroxy ethyl cellulose, methyl cellulose, hydroxy propyl cellulose, hydroxy propyl methyl cellulose, glyoxal modified materials of these, etc.) which are natural materials and their modified materials, and the synthetic materials such as poly vinyl alcohol and its derivatives, poly vinyl pyrrolidone, poly acrylamide and its co-polymers, poly acrylic acid and its co-polymers, vinyl methyl ether / maleic anhydride co-polymer, vinyl acetate / maleic anhydride co-polymer, etc. These macromolecules can be used alone or in combinations, and the concentration range for usage varies depending on the molecular weight, etc., of the macromolecule, however, it should be about 0.05 to 10 wt % in the concentrated wetting liquid composition, and preferably it should be 0.08 to 8 wt %.

The required surface tension of the water soluble, or the water - mixed- dispersable (this can be made to be water soluble) alcohol, glycol and / or polyol (component (□)) can be controlled by co-using the surfactant (component (/)). This mixture has the effect to give the uniform and thin wetability to the planographic print board.

In addition, it has the effect to prevent the soiling by the oil based ink on the roll surface of the roller of the water supply device system of the printer that is used to supply the wetting liquid, or the soiling of the wet roll, etc.

The alcohols and / or glycols that are effective in this invention are for example, n- propyl alcohol, ethylene glycol, propylene glycol, tri ethylene glycol, butylene glycol, hexylene glycol, tetra ethylene glycol, di-ethylene glycol, di-propylene glycol, glycerin, di-glycerine, tri methylol propane, methoxy ethanol, ethoxy ethanol, butoxy ethanol, 3- methoxy butanol,

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3-methyl-3-methoxy butanol, di-ethylene glycol mono methyl ether, di-ethylene glycol mono ethyl ether, di-ethylene glycol mono butyl ether, di-ethylene glycol mono propyl ether, tri-ethylene glycol mono methyl ether, tri-ethylene glycol mono butyl ether, tri-ethylene glycol mono propyl ether, tetra-ethylene glycol mono methyl ether, tetra-ethylene glycol mono ethyl ether, tetra-ethylene glycol mono butyl ether, and tetra-ethylene glycol mono propyl ether, etc., and these can be used suitably.

The above mentioned alcohols or glycols can be used alone or in combinations of two or more.

Due to the relationship with the dissolving phenomenon of the imaging part, the concentrated wetting liquid of this invention must include at least one of the above mentioned alcohols or glycols (component (□)) at 1 to 25 wt %, preferably at 5 to 20 wt %.

The surfactant (component (/)) that is used in this invention is the compound that is used to control the dynamic surface tension to be in the range of 30 to 50 dyne / cm, and to be concrete, ethylene oxide and / or the propylene oxide adduct of 2-ethyl-1,3-hexane diol, ethylene oxide and / or the propylene oxide adduct of 2,5-dimethyl hexane-2,5-diol, and as the acetylene glycol, the ethylene oxide and / or the propylene oxide adduct, of the 2,4,7,9-tetra methyl-5-decyne-4,7-diol, 2,5-dimethyl-3-hexyne 2,5-diol, 3-methyl-1-butyne-3-ol, 3-methyl-1-pentyne-3-ol, and the 3,6-di-methyl-4-octyne-3,6-diol, etc., can be used.

In this invention, the added number of moles of ethylene oxide and / or the propylene oxide is especially important, and it should be preferably in the range of 1 to 20 moles. When it exceeds 20 moles, the decrease in the dynamic surface tension is impaired, and it becomes difficult to give the good printing ability.



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In order to obtain the suitable surface tension, the concentrated wetting liquid of this invention should include at least one surfactant in the range of 0.2 to 50 wt %, and preferably it should be included in the range of 0.5 to 40 wt %.

The water soluble organic acid, inorganic acid and / or the salts of these (二)) have the effect of adjusting the pH of the wetting liquid or the effect of pH buffering, and the appropriate etching or prevention of corrosion of the planographic print board support body. The preferred organic acids are for example, citric acid, ascorbic acid, malic acid, tartaric acid, lactic acid, acetic acid, gluconic acid, acetic acid, hydroxy acid? (*this may be a typo, Translator*), oxalic acid, malonic acid, levulinic acid, sulfanilic acid, p- toluene sulfonic acid, phytic acid, and organic phosphonic acid, etc. Those that can be listed as the inorganic acids are for example, phosphoric acid, nitric acid, and sulfuric acid. In addition, the alkali metal salts, the alkali earth metal salts or the ammonium salts of these organic and / or inorganic acids can also be used suitably. These organic acids, inorganic acids and / or the salts of these can be used alone, or in combinations of two or more. The amount of the component (二) to be added into the concentrated wetting liquid of this invention must be considered in relation to the component (一), however, in order to buffer the pH change due to the mixing - in of the components that were included in the paper during the printing, or to maintain the acidic conditions, it should be 0.01 to 20 wt %, and it is preferred to use it in the acidic region where the pH value of the water- diluted- wetting- liquid is in the range of 3 to 7, however, it can be also used in the alkaline region which contains the alkali metal hydroxides the alkali metal salts of phosphoric acid, the alkali metal salts of carbonic acid, and the silicates, etc. and where the pH is 7 to 11

The water that is used in this invention can be any of tap water, well water, distilled water, and pure water, however, the usage of pure water is most preferred for preparing the concentrated wetting liquid. The amount of the water in the concentrated wetting liquid should be such that it is sufficient to dissolve the components (一), (二), (三) and (四), and

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other additional components that were added as desired, and preferably it should be 30 to 70 wt %.

A small amount of another surfactant may also be added in the concentrated wetting liquid of this invention. For example, those that can be listed as the anionic surfactants are, the salts of the fatty acids, salts of abietic acid, salts of hydroxy alkane sulfonic acids, salts of alkane sulfonic acids, salts of di-alkyl sulfone succinic acid, salts of the straight chain alkyl benzene sulfonic acids, salts of the branched chain alkyl benzene sulfonic acids, salts of alkyl naphthalene sulfonic acid, salts of alkyl phenoxy poly oxy ethylene propyl sulfonic acid, salts of polyoxy ethylene alkyl sulfo phenyl ether, the sodium salt of N- methyl -N-oleyl taurine, the di-sodium salt of N- alkyl sulfo succinic acid mono amide, complex salts of petroleum sulfones, sulfonated castor oil, sulfonated tallow oil, sulfuric acid ester salts of the fatty acid alkyl esters, alkyl sulfuric acid ester salts, polyoxy ethylene alkyl ether sulfuric acid ester salts, fatty acid mono glyceride sulfuric acid ester salts, polyoxy ethylene alkyl phenyl ether sulfuric acid ester salts, polyoxy ethylene styryl phenyl ether sulfuric acid ester salts, alkyl phosphoric acid ester salts, polyoxy ethylene alkyl ether phosphoric acid ester salts, polyoxy ethylene alkyl phenyl ether phosphoric acid ester salts, the partially saponificated styrene - maleic anhydride co-polymers, the partially saponificated olefin - maleic anhydride co-polymers, and the formalin poly condensed material of naphthalene sulfonic acid salt. Among these, the salts of di-alkyl sulfo succinic acid, the salts of the alkyl sulfuric acid esters and the salts of alkyl naphthalene sulfonic acid are especially preferred for use.

Those that can be listed as the non-ionic surfactants, are for example, polyoxy ethylene alkyl ethers, polyoxy ethylene alkyl phenyl ethers, polyoxy ethylene poly styryl phenyl ethers, polyoxy ethylene polyoxy propylene alkyl ethers, partial ester of glycerine fatty acids, partial esters of sorbitan fatty acid, partial esters of penta erythritol fatty acid, propylene glycol mono fatty acid esters, partial esters of the sucrose fatty acids, partial

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esters of the polyoxy ethylene sorbitan fatty acids, partial esters of polyoxy ethylene sorbitol fatty acids, poly ethylene glycol fatty acid esters, partial esters of the poly glycerin fatty acids, polyoxy ethylenated castor oil, partial esters of the polyoxy ethylene glycerin fatty acids, fatty acid di-ethanol amide, N, N- bis -2- hydroxy alkyl amines, polyoxy ethylene alkyl amines, tri ethanol amine fatty acid esters, and the tri alkyl amine oxides, etc. Among these, polyoxy ethylene alkyl phenyl ethers, and the polyoxy ethylene - polyoxy propylene block polymers, etc., are especially preferably used. Those that can be listed as the cationic surfactants are for example, the alkyl amine salts, the quaternary ammonium salts, polyoxy ethylene alkyl amines, and the poly ethylene poly amine derivatives, etc.

Considering a generation of bubbles, the content of these surfactants should be less than 10 wt %, preferably 0.01 to 3 wt %.

In addition, the chelation agent can be added too, into the concentrated wetting liquid of this invention. Normally, the concentrated wetting liquid of this invention is used after it is diluted with tap water or well water, etc., but the calcium ions, etc., give ill effects on printing, and sometimes it becomes the cause of the soiling of the printed material. In such cases, if the chelate forming agent is added, the above mentioned problem can be solved. The preferred chelate forming agents are for example, ethylene diamine tetra acetic acid, its potassium salt, its sodium salt; di-ethylene tri amine penta acetic acid, its potassium salt, its sodium salt; tri ethylene tetramine hexa acetic acid, its potassium salt, its sodium salt; hydroxy ethyl ethylene diamine tri acetic acid, its potassium salt, its sodium salt; nitrito tri acetic acid, its sodium salt; and the organic phosphonic acids such as 1 - hydroxy ethane -1, 1- di-phosphonic acid, its potassium salt, its sodium salt; and amino tri (methyl phosphonic acid), its potassium salt, its sodium salt, etc., or phosphono alkane tri carboxylic acid. The salts of the organic amines are also effective instead of the sodium salt or the potassium salt of the above mentioned chelate forming agents. The chelate

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agent that is selected should be able to stay in the concentrated wetting liquid stably, and also it should not inhibit the printability. The amount of the chelate compound that should be added into the concentrated wetting liquid should be 0.001 to 10 wt %, preferably 0.01 to 5 wt %.

In addition, the concentrated wetting liquid of this invention can contain various coloring agents, agents to eliminate the bubbles, and a rot proofing agent, etc. For example, the food color can be preferably used as the coloring agent. For instance, CI No. 19140 and 15985 as the yellow color, CI No. 16185, 45430, 16255, 45380, and 45100 as the red color, CI No. 42640 as the purple color, CI No. 42090 and 73015 as the blue color, and CI No. 42095 as the green color, can be listed. The silicon bubble eliminating agent is preferred for use as the bubble eliminating agent, and either one of the emulsion dispersion type and the solution type, can be used. The amount to be added should be preferably 0.001 to 0.01 wt %. Those that can be listed as the rot proofing agent are, phenol and its derivatives, formalin, imidazole derivatives, sodium dehydro acetate, 4-iso thiazoline -3-on derivatives, benz triazol derivatives, amidine guanidine derivatives, quaternary ammonium salts, derivatives of pyridine, quinoline and guanidine, etc., diazine, triazol derivatives, oxazol, and xazine derivatives, etc. The preferred amount to be added, is an amount which can have the stable effect to control the bacteria, fungus, yeast, etc. Although it is different depending on the type of the bacteria, fungus or yeast, the amount should be preferably in the range of 0.01 to 4 wt % of the concentrated wetting liquid, and in order to give the controlling effect for the various funguses or bacterias, it is preferred to co-use two or more rot proofing agents together. A good example of such co-usage is listed in Patent Application Kokai No. S55-73603.

The above mentioned component includes 30 to 70 wt % of water soluble and water-mixed components where these are dissolved in water, preferably in desalted water, namely pure water.

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5 to 30 mL of the concentrated wetting liquid of this invention should be added into 1 L of water, to be used as the wetting liquid for the printing machine.

The planographic print board on which the concentrated wetting liquid of this invention is used, can be various planographic boards, for instance the photo sensitive planographic board (PS board), the plane - concave board, the multi-layer metal board such as the bimetal, tri metal, etc., the direct drawing master, the electro photograph planographic boards, etc.

The above mentioned photo sensitive planographic print board (PS board) is such that the photo sensitive layer that includes the photo sensitive composition is provided on the support body which has a hydrophilic surface. Those that can be listed as the said photo sensitive composition are, the photo sensitive composition that contains a diazo compound; the photo sensitive composition that contains an azide compound such as those indicated in the English Patent No. 1,235,281, and the English Patent No. 1,495,861; the photo sensitive composition that contains a light cross linking photo polymer such as those indicated in US Patent No. 3,860,428; the photo sensitive composition that contains the light polymerizing type photo polymer such as those indicated in US Patent No. 4,072,528 and US Patent No. 4,072,527; the light photo conductive type composition such as those indicated in Patent Application Kokai No. S56-19063 and Patent Application Kokai No. S56-29250; and the halogenated silver emulsion compositions such as those indicated in Patent Application Kokai No. S52-62501 and Patent Application Kokai No. S56-111852.

Among these, the photo sensitive compositions which include a diazo compound, have excellent ability to store the photo sensitive layer, good developing performance such as the development latitude, etc., good image performance such as the image quality, etc., excellent printing performance such as the ink attaching ability, good lipid sensitive ability

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and good wear resistance, etc., and the pollution level of the developing liquid that is used with these is low, and thus, it is generally excellent on the whole, therefore, it is used preferably.

The photo sensitive compositions that include a diazo compound, can be divided into the negative types and the positive types.

The negative type photo sensitive composition that includes a diazo compound, contains a photo sensitive diazo compound and preferably a macro molecular compound, and those that have been known until now, can be used as the photo sensitive diazo compound. The preferred ones are, for example, the salts of the diazo resins which are soluble in organic solvents, for instance the salt with the condensed material of p- diazo phenyl amine and formaldehyde or acetaldehyde and hexa fluoro phosphate, the salt with 2- hydroxy -4- methoxy benzophenone -5- sulfonate, and the salt with dodecyl benzene sulfonate, etc.

The macromolecular compounds that are used preferably are for example, the acrylic acid or methacrylic acid co-polymers, crotonic acid co-polymers, itaconic acid co-polymers, maleic acid co-polymers, the cellulose derivatives which have a carboxyl group in their branch chain, the poly vinyl alcohols which have a carboxyl group in their branch chains, the hydroxy alkyl acrylate or methacrylate co-polymers which have a carboxyl group in their branch chain, and the unsaturated poly ester resins which have a carboxyl group, etc.

An already known diazo compound can be used as the positive type photo sensitive composition, and the representatives are the o- quinone diazides, and the preferred one is the o- naphtho quinone diazide. Among the o- naphtho quinone diazide compounds, the o- naphtho quinone diazide sulfonic acid ester or o- naphtho quinone diazide carboxyl acid ester of the various hydroxy compounds, and the o- naphtho quinone diazide sulfonic acid amide or o- naphtho quinone diazide carboxyl acid amide of the aromatic amino

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compounds, are especially preferred. The preferred hydroxy compounds that can be listed are, for example, the poly condensed resin between the phenols and compounds which contain a carbonyl group. The said phenols are for example, the phenol, creosol, resorcin, and pyrogallol, etc. The said compounds that contain a carbonyl group are for example, the formaldehyde, benzaldehyde and acetone, etc. The preferred hydroxy compounds that can be listed are, the phenol • formaldehyde resin, creosol • formaldehyde resin, pyrogallol • acetone resin, and the resorcin • benzaldehyde resin.

The representative concrete examples of the o-quinone diazide compounds are, the ester between benzo quinone -(1, 2)- diazide sulfonic acid or naphtho quinone -(1, 2)- diazide sulfonic acid, and phenol • formaldehyde resin or the creosol • formaldehyde resin; the ester between naphtho quinone -(1, 2)- diazide -(2) -5- sulfonic acid and the resorcin • benz aldehyde resin, which was described in Patent Application Kokai No. S56-1044; the ester between naphtho quinone -(1, 2)- diazide sulfonic acid and the pyrogallol • acetone resin, which was described in US Patent No. 3,635,709; and the ester between the naphtho, quinone -(1, 2)- diazide -(2) -5- sulfonic acid and the resorcin - pyrogallol - acetone co-poly condensed material, which was described in Patent Application Kokai No. S55-76346. In addition, the useful o- quinone diazide compounds that can be listed are, the ester reacted material of the polyester that has a terminal hydroxy group, and the o-naphtho quinone diazide sulfonyl chloride, which was described in Patent Application Kokai No. S50-117503; the ester reacted material of the homo polymer of hydroxy styrene or the co-polymer with another co-polymerizable monomer, and o- naphtho quinone diazide sulfonyl chloride, which was described in Patent Application Kokai No. S50-113305; the ester between the bis phenol • formaldehyde resin and o- quinone diazide sulfonic acid, which was described in Patent Application Kokai No. S54-29922; the condensed material between o- quinone diazide sulfonyl chloride and the co-polymer of an alkyl acrylate, an acryloyl oxy alkyl carbonate and a hydroxy alkyl acrylate, which was described in US Patent No. 3,859,099; the reaction product between the co-polymer of

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styrene and a phenol derivative, and o-quinone diazide sulfonic acid, which was described in Patent Application Kokoku No. S49-17481; the amide between the co-polymer of p-amino styrene and a monomer that can co-polymerize with it, and o-naphtho quinone diazide sulfonic acid or o-naphtho quinone diazide carboxylic acid, which was described in US Patent No. 3,759,711; and in addition, there are the ester compounds between poly hydroxy benzo phenone and o-naphtho quinone diazide sulfonyl chloride.

These o-quinone diazide compounds can be used alone, however, it is preferred if it is mixed with an alkali soluble resin and this mixture is provided as the photo sensitive layer. The suitable alkali soluble resins include the novolac type phenol resin, and to be concrete, this includes the phenol formaldehyde resin, creosol formaldehyde resin, and the phenol • creosol formaldehyde co-polycondensed resin that was indicated in Patent Application Kokai No. S55-57841. Especially, as was indicated in Patent Application Kokai No. S50-125806, if the above mentioned phenol resin is co-used with the condensed material of phenol or creosol which was substituted with an alkyl group with 3 to 6 carbon atoms, and formaldehyde, such as the t-butyl phenol • formaldehyde resin, it is even better.

In addition, the alkali soluble resins other than the above mentioned alkali soluble novolac type phenol resin, can be blended too depending on the necessity. For example, the styrene - acrylic acid co-polymer, the methyl methacrylate - methacrylic acid co-polymer, an alkali soluble poly urethane resin, an alkali soluble vinyl type resin and the alkali soluble poly butyral resins, etc., can be listed.

The content of the o-quinone diazide compound should be preferably 5 to 80 wt % of the total solid portion of the photo sensitive composition, and more preferably it should be 10 to 50 wt %. The content of the alkali soluble resin should be preferably 30 to 90 wt % of the total solid portion of the photo sensitive composition, and more preferably it should be



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50 to 85 wt %.

The layer of the photo sensitive composition can be provided in multiple layers too, and if necessary, the additives such as the dye, the plasticizer, or the component that can give better print out performance, can be added too.

The amount of the above mentioned photo sensitive composition to be applied that is provided on the support body, should be 0.1 to 7 g / m<sup>2</sup>, and preferably it should be 0.5 to 4 g / m<sup>2</sup>.

If necessary, the under coat layer can be provided between the support body and the photo sensitive composition layer, and such under coat layer can be the metal salt and the hydrophilic cellulose which was described in Patent Application Kokoku No. S57-16349, the poly vinyl sulfonic acid described in Patent Application Kokoku No. S46-35685,  $\beta$  - alanine is described in Patent Application Kokai No. S60-149491, or the hydrochloric acid salt of tri ethanol amine that was described in Patent Application Kokai No. S60-232998.

Those that can be used as the support body that is used for the photo sensitive planographic print board that is used in this invention, are for example, aluminum (this includes the aluminum alloys too), paper, plastic (for example, poly ethylene, poly propylene, poly ethylene tere phthalate, cellulose di- acetate, cellulose tri- acetate, cellulose propionate, poly vinyl acetal, poly carbonate, etc.), and the composite support body where aluminum is laminated or vapor deposited on metals such as zinc or copper, etc.

The surface of the aluminum material should preferably be rough surface treated to increase the water retaining ability, and to improve the attachability with the photosensitive layer.

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The surface roughing method can be the brush polishing method that is known commonly, the ball polishing method, electrolysis etching, chemical etching, liquid honing, sand blasting, etc., and the combinations of these. The preferred methods are the brush polishing method, electrolysis etching, chemical etching and liquid honing. Among these, the surface roughing which includes the use of electrolysis etching is especially preferred. The electrolytic solution that includes hydrochloric acid, nitric acid or a mixture of these is preferred as the electrolytic bath that is used during the electrolytic etching. In addition, the aluminum plate of which the surface was rough treated, will be desmat? (*phonetically written, Translator*) treated with an aqueous solution of acid or alkali, if necessary. The aluminum plate obtained like this should be preferably cathode oxidation treated, especially the method of treating it in a sulfuric acid or phosphoric acid bath is preferred. In addition, if necessary, the pore sealing treatment, or the surface treatment by submersion in an aqueous solution of potassium fluorinated zirconate, can be done.

Thus, the obtained PS board is exposed by the light source with a rich active light beam such as a carbon arc lamp, a mercury lamp, a metal halide lamp, a tungsten lamp, etc., through the transparent original pattern, and thereafter, it is developed in the developing process which is the wet treatment.

The developing liquid that is used in the above mentioned development treatment process is an alkaline solution of which the main solvent is water, and depending on the necessity of the alkali agent, those which contain an organic solvent, an anionic surfactant and inorganic salts, etc., can be used.

In addition, if necessary, the developing liquid can contain the bubble eliminating agent, the wetting agent, etc., too, and that will be useful.

Various already known methods can be used as the method to develop the PS board that

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was image exposed by the above mentioned developing liquid. To be concrete, these are for example, the method in which the image exposed PS board is submerged in the developing liquid, the method in which the developing liquid is sprayed from multiple nozzles onto the photo sensitive layer of the PS board, the method in which the photo sensitive layer of the PS board is wiped with a sponge that is wetted with the developing liquid, and the method in which the developing liquid is roller coated on the surface of the photo sensitive layer of the PS board. Also, after the developing liquid is applied on the photo sensitive layer of the PS board, the surface of the photo sensitive layer can be lightly scrubbed too, with a brush, etc.

After the above mentioned develop- treatment, the water washing, rinsing, and desensitizing treatment, etc., can be combined, and the develop - treatment of the PS board can be completed.

The concentrated wetting liquid of this invention is normally diluted with water when it is used as the wetting liquid, and with this, the printing which does not have the foundation soiling or the oxidation soiling, and which does not have the roller boldness or a decrease in the ink concentration due to the excessive emulsifying phenomenon of the ink and water, can be performed, and the good printed material with excellent dot form, can be obtained, and the printing can become efficient, and the productivity can be improved. In addition, in the case when it is used as the wetting liquid, especially in the case when it is used in the printing machine of the continuous water feeding method which is represented by the "darigien?" (*phonetically written, Translator*) method, the good printed material can be obtained without using iso propyl alcohol, however, even if a small amount of iso propyl alcohol, for example 1 to 15 %, is co-used, there is no problem in the print quality.

When the above mentioned concentrated wetting liquid is diluted with water, it should be

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diluted with at least 90 wt %, preferably 95 wt % of water, and the wetting liquid with a solid portion of 0.01 to 1 wt % should be made, and preferably this should be used for the planographic printing process. The most preferred wetting liquid of the above mentioned composition should have the following physical properties when it is diluted with water to be used, namely, the dynamic surface tension should be preferably in the range of 30 to 50 dyne / cm, and the viscosity should be 1.1 to 5.0 centipoise.

The wetting liquid of this invention has good wetability for the planographic print board, and the soil on the non- imaging part of the print board or the "bleeding" can be prevented. Also, the loss of the paper can be greatly decreased, so that it is advantageous from an economic viewpoint too.

#### [Actual Examples]

Next, this invention will be explained in further detail referring to the actual examples. Here, % indicates wt %, unless specifically noted otherwise.

#### Example 1

##### Concentrated wetting liquid

- \* Pure water : 52.69 %
- \* Carboxy methyl cellulose (CMC) (commercial name; Celogen? (*spelling uncertain, Translator*) 5A, a product of Daiichi Kogyo Yakuhin K.K.) : 1.8 %
- \* Magnesium nitrate ( $\text{SH}_2\text{O}$ ) : 1 %
- \* Sodium nitrate : 0.5 %
- \* Phosphoric acid (85%) : 3 %
- \* Ethylene oxide 1 to 5 adduct of 2-ethyl -1, 3- hexane diol : 30 %
- \* Propylene glycol : 10 %
- \* Rot proofing agent (Proxel? (*spelling uncertain, Translator*) CRL) < a product of 1C1 Japan K.K. > : 1 %

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\* Bubble eliminating agent < KS 607 (silicon denatured oil type) (a product of Shin'etsu Kagaku Kogyo K.K.) : 0.01 %

In order to prepare the concentrated wetting liquid, the CMC was added into pure water, a small amount at a time while mixing, and it was dissolved, and after it was completely dissolved, the rest of the components were added in order, and it was stirred until each component was completely dissolved.

The concentrated wetting liquid of the above mentioned composition was diluted with water 1 : 40, and thus, the wetting liquid to be used was prepared.

On the other hand, the FPS (cathode oxidation multi-grain type positive type PS board, made by Fuji Shashin Film K.K.) was image - exposed as the planographic print board, and the development and the rubber spreading were done by using the PS automatic developing machine 900D, the positive developing liquid A with the following composition, and the finisher gum with the following composition (both are the product of Fuji Shashin Film K.K.).

**Positive developing liquid A :**

- \* Sodium silicate in which the mole ratio of  $\text{SiO}_2$  /  $\text{Na}_2\text{O}$  is (1.1) : 2 g
- \* Sodium ethylene diamine tetra acetate •  $4\text{H}_2\text{O}$  : 0.1 g
- \* Water : 97.9 g

**Finisher gum composition**

Water phase (A)

Gum Arabic	4 g
Dextrin	16 g
Phosphoric acid (85 %)	0.2 g

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Water	75 g
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## Oil phase (B)

Sodium di-alkyl sulfo succinate	1 g
Rosin ester	0.5 g
Di- octyl phthalate	3 g

The liquid (B) was added into the liquid (A), and the emulsion liquid was made.

Thereafter, it was installed on the Offset printer, Harris Oleria 125 ( made by Marubeni Harris Insatsu Kikai K.K.) using the "Darlglen?" method, and the above mentioned wetting liquid and ink (Apex? (*spelling uncertain, Translator*) G scarlet? S, a product of Dainihon Ink Kagaku Kogyo K.K.) were set, and the characteristics of the wetting liquid were evaluated for the following items.

**a. Soiling of the metering roll :**

The soiling due to the ink attaching on the metering roll was checked.

Good	A
Slightly bad	B
Bad	C

**b. Bleeding nature :**

After 5000 sheets and 10,000 sheets were printed using the ink (Apex? G scarlet S, a product of Dainihon Ink Kagaku Kogyo K.K.), the operation of the printing machine was stopped, and the ink blotting of the image line part into the non- imaging part was checked.

Almost no blotting	A
Slight blotting	B
a great deal of blotting	C

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## c. Emulsifying nature :

After 10,000 sheets were printed, the emulsifying condition of the ink on the ink roll was checked.

Good	A
Slightly bad	B
Bad	C

## d. Continuous stability :

10,000 sheets were printed using the fresh water as the wetting liquid, and the amount of the wetting liquid with which the soiling does not occur (the minimum water used) was obtained, and the printing was done by using the various wetting liquids at the same amount as this minimum of water used, and the number of printed sheets until the soiling occurred in the printed material, was checked.

More than 10,000 sheets	A
10,000 to 3,000 sheets	B
Less than 3,000 sheets	C

As the result of testing the wetting liquid of this invention, all four of (a) the soiling of the metering roll, (b) bleeding, (c) emulsifying, and (d) continuous stability, are good, and the good printed material was obtained.

Also, the wetting liquid was circulated for 10 hours continuously without compensation, and the change in the concentration of each component was checked, but there was almost no change, and it has excellent stability.

**Comparison 1**

The plate making printing prescription (presented by the Printing Academy) was prepared as the wetting liquid.

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Magnesium nitrate	113 g
Phosphoric acid (85 %)	37 cc
Water added to	3785 cc

50 cc of the above mentioned etching liquid was diluted with water to 3785 cc, and in addition, 30 cc of the gum Arabic liquid (14 ° Be') was added, and this was the wetting liquid, and 15 % of iso propyl alcohol was added, and the comparison liquid was prepared. The wetting characteristics were checked the same as in Example 1. As the result, a fine ink attaching defect was observed in the fine line part of the imaging area of the planographic print board. There were no problems with (a) the meter ring soil, however, (d) the continuous stability, was poor.

Also, it was circulated continuously for 10 hours at 15 °C without compensating the wetting liquid; and the change in each component was checked. As the result, the iso propyl alcohol was lower by 20 %, compared with the added amount.

#### Example 2

The concentrated wetting liquid with the following composition was prepared the same as in Example 1, and the characteristics of the concentrated wetting liquid were evaluated.

- \* Pure water : 46.4 %
- \* Glyoxal modified material of the cellulose derivative [methoxyl group / hydro propoxyl group = (19 to 24 %) / (4 to 12 %)] : 6 %
- \* NaOH : 0.1 %
- \* Nickel nitrate : 2 %
- \* antimony (I) citrate : 1.5 %
- \* Phosphoric acid (85 %) : 2 %
- \* ethylene oxide adduct (3 to 10 mole) of 2, 4, 7, 9, - tetra methyl -5- decyne -4, 7- diol :



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20 %

- \* di-ethylene glycol : 10 %
- \* butoxy ethanol : 10 %
- \* rot proofing agent [commercial name, Deltop? (*spelling uncertain, Translator*), a product of Takeda Yakuhin K.K.] : 2 %

**Example 3**

- \* Pure water : 54.2 %
- \* Glyoxal modified material of the cellulose derivative [this is the same as in Example 2.] : 1.3 %
- \* Vinyl methyl ether / maleic anhydride co-polymer (commercial name: Gantored? (*spelling uncertain, Translator*) S-95) : 0.5 %
- \* KOH : 2 %
- \* Zinc nitrate : 1 %
- \* 1- hydroxy ethylidene 1, 1- di-phosphonic acid : 2 %
- \* Phosphoric acid (85 %) : 2 %
- \* ethylene oxide adduct (2 to 4 mole) / propylene oxide adduct ( 1 to 2 mole) of 2- ethyl -1, 3- hexane diol : 20 %
- \* Propylene glycol : 10 %
- \* 3- methyl -3- methoxy butanol : 5 %
- \* Rot proofing agent [commercial name, Biohope, a product of KI Kasei K.K.] : 2 %

**Example 4**

- \* Pure water : 63.5 %
- \* Carboxy methyl cellulose (CMC) commercial name: Celogen 5A, a product of Daiichi Kogyo Yakuhin K.K.) : 1 %
- \* Carboxy methyl modified starch : 1 %
- \* Magnesium nitrate : 1.5 %

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- \* Ethylene oxide (3 to 5 mole) adduct of 2 - ethyl -1, 3- hexane diol : 15 %
- \* Ethylene oxide (8 to 12 mole) adduct / propylene oxide (1 to 2 mole) adduct of 3, (5)-di-methyl -4- octyne -3, (5)-diol : 5 % *How to make?*
- \* Ethylene oxide / propylene oxide block co-polymer commercial name : Purulonika or P-85, a product of Asahi Denka K.K.) : 1 %
- \* Di- propylene glycol : 9 %
- \* Rot proofing agent, formalin (37 %) : 3 %

Table 1. Characteristics of Wetting Liquid

	Example 2	Example 3	Example 4	Comparison 1
(a) metering roll soil	A	A	A	A
(b) Bleeding nature	A	A	A	A
(c) Emulsifying nature	A - B	A - B	A - B	A
(d) Continuous stability	A	A	A	B
Other Composition change in the running	almost no change	almost no change	almost no change	large change.

A : good  
B : Poor

The FNS (cathode oxidation multi grain type negative type PS board, made by Fuji Shashin Film K.K.) was exposed as the print board, and the development and the rubber spreading were done using a PS automatic developing machine 800H, the negative developing liquid with the following composition, and the negative finisher gum with the following composition (both are the products of Fuji Shashin Film K.K.). Thereafter, using the concentrated wetting liquid of Examples 1 to 4, the printing was evaluated with the Offset printer, Harris Oleria? (*spelling uncertain, Translator*) 125 ( made by Marubeni Harris? Insatsu Kikai K.K.). As the result, all showed good performance, the same as in Table 1.

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**Negative developing liquid Composition :**

- \* Mono ethanol amine : 10 g
- \* Sodium iso propyl naphthalene sulfonate : 20 g
- \* Benzyl alcohol : 30 g
- \* Benzoic acid : 3 g
- \* Water added to 1000 mL

**Negative finisher gum composition****Aqueous solution C**

Gum Arabic	4 g
Dextrin	16 g
Phosphoric acid (85 %)	0.05 g
Water	75 g

**Aqueous solution D**

Sodium di-alkyl sulfo succinate	1 g
Di- butyl phthalate	2 g
Poly oxy ethylene nonyl phenyl ether (HLB = 8)	1g
Sorbitan mono oleate	1 g

The aqueous solution D was added into the aqueous solution C, and the emulsion liquid was made.

**[Effect of the Invention]**

The concentrated wetting liquid for the planographic print board of this invention, is not toxic, the working environment does not become polluted by its use, and it does not create a fire hazard, so that a local ventilation facility is not necessary. In addition, it has excellent wetting liquid characteristics such as preventing the soiling of the metering roll,

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the bleeding nature, the emulsifying nature, and the continuous stability, etc., and the generation of bubbles is small, and the printing can be performed with stability.

*[The remainder of the document was corrections. These corrections were all made in the translation, Translator]*